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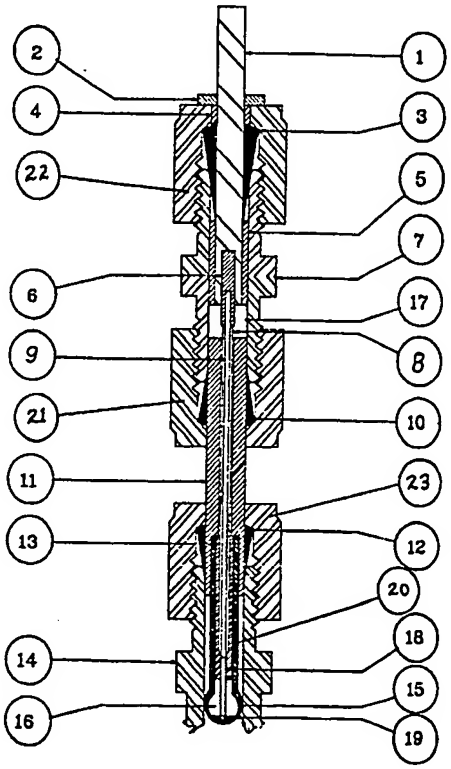
(54) High-pressure glass electrode

(57) A high pressure glass electrode comprises a generally spherical or part-spherical glass container 15 formed of a glass which is sensitive to the ions to be determined, a metallic electrode 18 extending into the interior of the glass container, and an electrolyte 16 sealed within the container and wholly filling the available space within the container. The electrolyte may be a gel or paste. The electrode is suitable for carrying out electrochemical analysis in high-pressures up to 400 bar.



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The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1990.

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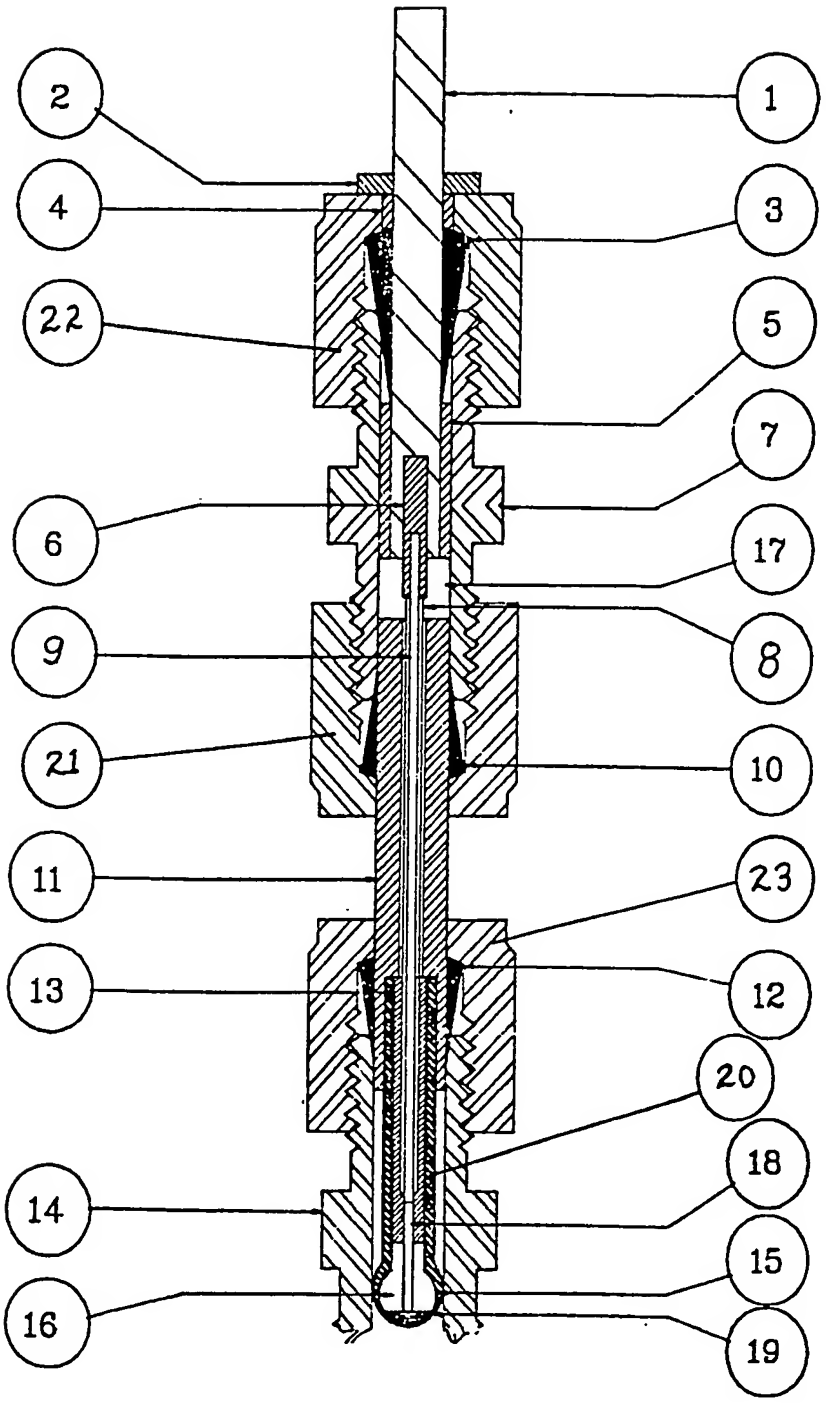

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High Pressure Glass Electrode.

The present invention is a glass electrode for use in electrochemical analysis, which is suitable for use at significantly elevated pressures.

Glass electrodes are of value in a range of different electrochemical analyses, for determining concentrations of ions such as sodium, potassium and chloride and for monitoring pH levels, for example. However hitherto available glass electrodes can only be used at atmospheric pressure or at best at pressures below about 2 atmospheres and this pressure limitation greatly restricts their range of potential applications. Thus, by way of example, existing glass electrodes would be valuable in power generation applications, for monitoring ion concentrations in boiler water, and for on-shore and off-shore underground and sub-sea applications if they could survive exposure to higher pressure conditions without damage and without loss of performance.

It is therefore an object of the present invention to provide an analytical electrochemical glass electrode which can be used at pressures which are significantly higher than those at which most, and possibly all, presently-available such electrodes can be used.

The glass electrode according to the present invention comprises a generally spherical or part-spherical glass container formed of a glass which is sensitive to the ions to be determined, a metallic electrode extending into the interior of the glass container, and an electrolyte sealed within the container and wholly filling the available space within it. By virtue of these aforementioned features of the glass electrode according to the invention, the electrode can be used to monitor ion concentrations in situations and locations where the external pressure upon the glass surface of the electrode is as high as many tens or even several hundreds of atmospheres.

It is believed that the success of the glass electrode according to the invention in meeting the need for one which can be used at significantly elevated pressures can be attributed to the use of a glass container, for example a bulb, which is sealed and wholly filled with a material, namely the electrolyte, which is incompressible at the desired operating pressures. By this structure, the external pressure, which otherwise would readily

cause the glass to collapse inwardly, is borne by the electrolyte and the electrode is therefore able to function normally even at high pressures.

The glass container. as indicated, is formed of a glass which is selected to be sensitive to the ions under investigation, for example a pH-sensitive glass, which is preferably of low electrical resistance. The container is spherical or part-spherical and is preferably in the form of a bulb or of a short cylinder with a rounded end. The thickness of the glass may be very small, for example as little as a fraction of a millimetre, with the spherical part of the container having a diameter as low as 2 millimetres or less if desired.

Electrical contact with the electrolyte in the interior of the glass container is by means of a metallic electrode. The metallic electrode is preferably a metal wire, for example of silver or platinum depending on the nature of the electrolyte and of the ion under investigation. The metallic electrode within the electrolyte may in turn be electrically connected outside the electrolyte to a conductor of a different metal, for example of brass or steel.

The electrolyte which is used is determined by the ion being monitored, using conventional electrochemical analytical methods, and the selection of the electrolyte as such is not itself a major feature of the present invention. The selected electrolyte may be used in liquid form but more preferably is in the form of a gel or paste.

The electrolyte in the glass electrode according to

the present invention must fill the whole of the available space within the glass container, leaving no air or other gaseous voids in that space. After the introduction of the electrolyte, the container is sealed, for example by means of a curable filler material.

Additional support and/or protection may be given to the glass electrode by fitting the whole above -described electrode assembly into a carrier, especially a protective steel carrier structure, which leaves only the operative curved surface of the glass container exposed to the analyte. Rearward of that exposed surface, the carrier should be sealed to prevent ingress of analyte under pressure.

The invention will now be further described, by way of example only, with reference to the accompanying drawing, which is a sectional view of one preferred embodiment of the high pressure glass electrode according to the present invention.

The illustrated glass electrode, which is designed for determining pH levels, comprises a thin bulb 15 of pH-sensitive glass of low electrical resistance, fused on to a high-electrical-resistance glass stem 20. A metallic electrode in the form of a short length 18 of silver wire, in turn soldered to a conductor 9 of copper wire which is covered with a curable resin to provide insulation, projects into the interior of the bulb 15 and abuts a pad 19 of cotton wool which affords it additional support. The conductor 9 is enclosed throughout a major part of its

length by non-conductive tubing 8 and the annular space between the tubing 8 and the interior of the glass stem 20 is filled with a PTFE or silicone filler material 13 which was cured in situ while the electrode assembly was being constructed.

The tip of the silver wire 18 has a coating of silver chloride. The space 16 within the bulb 15 and below the filler 13 is wholly filled with an electrolyte in the form of a gel or paste.

At its end remote from the bulb 15, the copper wire conductor 9 is soldered to a brass connector 6, upon which is screwed a stainless steel connector 1, by means of which the glass electrode is connected into the electrical circuit by means of which the signal from the electrode is monitored.

The glass stem 20 and the copper conductor 9 and surrounding tubing 8 are mounted within a stainless steel carrier 11 and the carrier itself is supported upon the end of the connector 1 by means of a fitting 7. The carrier 11 and connector 1 are supported within the fitting 7 by ferrules 10 and 3 respectively, both of polyether ether ketone (PEEK), which are retained in place by nuts 21 and 22 respectively.

The connector 1 is insulated with respect to the fitting 7 and nut 22 by insulating sleevings 5, 4 respectively, which are shrunk-fit in position, and the annular space 17 between the carrier 11 and

the connector 1 is filled with a silicone sealant. The upper end of the electrode assembly is further sealed around the connector 1 by means of a PTFE washer 2.

In use, the electrode is mounted in a stainless steel T-piece 14 (only one limb of which is shown in the drawing) by means of a further PEEK ferrule 12, retained and pressured by a nut 23. Analyte flows through the T-piece 14 and its pH level is therein monitored by the glass electrode.

The illustrated glass pH electrode has been successfully tested experimentally at pressures up to 400 bar (6000 pounds/in^2) without leaking. A linear response was obtained at pH values within the range from 4 to 9 inclusive. This performance was maintained at temperatures from minus 15 to plus 70 degrees Centigrade.

The glass electrode according to the present invention may be very small. For example, the glass bulb 15 in the illustrated embodiment may have a diameter of as little as 2 millimetres and the overall length of the glass electrode may then be as little as 3 centimetres. Where circumstances require it, these dimensions may be reduced even further. The design is simple and lends itself to manufacture in quantity at low cost.

Because the glass electrode according to the invention is suitable for carrying out electrochemical analysis in high-pressure locations,

it may be used in such diverse operations as power generation and geothermal surveys. It is suitable for use in monitoring ion levels in boiler water and, in sub-sea operations, for monitoring corrosion and environmental conditions. The electrode may further be used for in-situ analysis in bore-holes and also in geological surveys. It is also of specific value for use in the oil industry and in connection with the storage of nuclear fuel.

CLAIMS

1. A glass electrode comprising a generally spherical or part-spherical glass container formed of a glass which is sensitive to the ions to be determined, a metallic electrode extending into the interior of the glass container, and an electrolyte sealed within the container and wholly filling the available space within the container.

2. A glass electrode as claimed in claim 1, wherein the glass container is in the form of a bulb or short cylinder having a rounded end.

3. A glass electrode as claimed in either claim 1 or claim 2, wherein the metallic electrode comprises a metal wire.

4. A glass electrode as claimed in claim 3, wherein the metallic electrode comprises a silver or platinum wire.

5. A glass electrode as claimed in any of the preceding claims, wherein the metallic electrode is electrically connected outside the

electrolyte to a conductor of a different metal.

6. A glass electrode as claimed in any of the preceding claims, wherein the electrolyte is in the form of a liquid.

7. A glass electrode as claimed in any of claims 1-5, wherein the electrolyte is in the form of a gel or a paste.

8. A glass electrode as claimed in any of the preceding claims, wherein the container is sealed by means of a curable filler material after the introduction of the electrolyte into the container.

9. A glass electrode as claimed in any of the preceding claims, wherein the glass electrode is fitted into a protective carrier.

10. A glass electrode substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawing.

Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9222376.7
Relevant Technical Fields (i) UK Cl (Ed.L) G1N (NBEG) (ii) Int Cl (Ed.5) G01N	Search Examiner D J MOBBS Date of completion of Search 25 November 1993
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii)	Documents considered relevant following a search in respect of Claims :- 1-10

Categories of documents

X:	Document indicating lack of novelty or of inventive step.	P:	Document published on or after the declared priority date but before the filing date of the present application.
Y:	Document indicating lack of inventive step if combined with one or more other documents of the same category.	E:	Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A:	Document indicating technological background and/or state of the art.	&:	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
Y	WO 85/02021 A1	(ORION RESEARCH) see particularly Figures 1 and 3D.	2-4,6
X,Y	US 4519890	(HORIBA) see particularly Figure 3.	X:1,5,6,7,9 Y:2-4,6
X	US 4485001	(BECKMAN)	1-4,7,8

Databases:The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).